



This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

- + *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
- + *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
- + *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
- + *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at <http://books.google.com/>

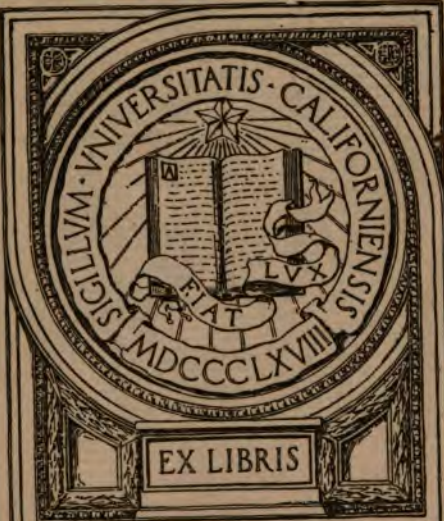


QB 50 733

QD
305
A4W5

91453 01

EXCHANGE



EX LIBRIS

27

A Study of the Reactions of Normal Butyl Mercaptan and Some of its Derivatives

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE RE-
QUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIV. OF
CALIFORNIA

BY
THOS. C. WHITNER, JR.

June, 1920



EASTON, PA.:
ESCHENBACH PRINTING COMPANY
1921

CI-20E
HAWIS

CONTENTS

Acknowledgment.....	2
Introduction.....	3
Experimental:	
Reactions of Butyl Mercapto-ethyl Alcohol.....	4
Reactions with Alkyl Halides.....	6
Reactions with Aldehydes and Ketones.....	6
Sulphones.....	7
Mercuric Iodine Derivatives.....	8
Discussion.....	9
Biography.....	10

462004

ACKNOWLEDGMENT.

This investigation was undertaken at the suggestion of Professor Reid and carried out under his direction. I gladly avail myself of this opportunity to express to him my sincere appreciation of the help which he gave. I wish also to thank Professors Frazer, Patrick, and Lovelace for instruction and encouragement received from them.

A SULFIDE ALCOHOL, OR BUTYL MERCAPTO-ETHYL ALCOHOL.

In a recent article from this laboratory,¹ the acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{COOH}$, was studied with respect to the influence of the sulfur atom on the chemical and physical properties. In the present investigation, the corresponding alcohol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$, has been studied with the same object in view.

This alcohol is obtained readily by the action of ethylene chlorohydrine on the sodium salt of butyl mercaptan in water solution. It is a colorless oil boiling at $92-3^\circ$ at 3 mm. In its physical properties and in its reactions, it resembles one of the higher alcohols, though some differences are found. Its odor suggests a higher alcohol and a sulfide, though the odor of its acetate is much more like that of an acetate of a higher alcohol. The chloride and bromide are readily prepared from the alcohol by the usual methods, but it shows very slight tendency to combine with phthalic anhydride. The sulfur atom appears to exercise somewhat the same influence on the mobility of the groups in the β -position as in the sulfide acid and in mustard gas, though the influence is less evident here. The acetate of this alcohol is stable, while the diacetate corresponding to mustard gas is very unstable.

From the bromide, $\text{BuSCH}_2\text{CH}_2\text{Br}$, the sulfide, $\text{BuSCH}_2\text{CH}_2\text{SBu}$, was readily obtained, but the corresponding sulfide ether, $\text{BuSCH}_2\text{CH}_2\text{OEt}$, could not be prepared by heating the bromide with sodium ethylate, vinyl-butyl sulfide, $\text{BuSCH} : \text{CH}_2$, was formed instead. This substance added hydrobromic acid readily to give the original bromide instead of the secondary bromide, BuSCHBrCH_2 , which we desired.

The properties of the alcohol and its derivatives are brought together in the following table.

TABLE I.

Compound.	B. p.	d_0^0 .	d_{25}^{25} .	$n_D^{20^\circ}$.
$\text{BuSCH}_2\text{CH}_2\text{OH}$	$92-3^\circ$ at 3 mm.	0.9828	0.9693	1.4800
$\text{BuSCH}_2\text{CH}_2\text{OCOCH}_3$	84° at 4 mm.	1.0043	0.9875	1.4648
$\text{BuSCH}_2\text{CH}_2\text{Cl}$	68° at 6 mm.	1.0315	1.0101	1.4825
$\text{BuSCH}_2\text{CH}_2\text{Br}$	74° at 3 mm.	1.2308	1.2089	1.6740

¹ Uyeda and Reid, *J. Am. Chem. Soc.*, **42**, 2385 (1920).

Experimental.

The Alcohol, Butyl Mercapto-ethyl Alcohol.—To 40 g. of caustic soda and 90 g. of butyl mercaptan dissolved in 250 cc. of water, 80 g. of chlorohydrine was added. The mixture was boiled under a reflux condenser for one hour and distilled with steam to eliminate impurities. The alcohol remained behind; it was separated, dried, and distilled *in vacuo*. Yield, 108 g.

The Acetate, Butyl Mercapto-ethyl Acetate.—The alcohol was mixed with an equal amount of acetyl chloride and the mixture allowed to stand for some hours. The product was washed thoroughly with water, then dried over calcium chloride and distilled.

Analysis. Subs., 1.7100: 0.5441 g. KOH required for saponification. Calc.: 0.5448.

The Chloride, Butyl Mercapto-ethyl Chloride.—A mixture of 30 g. of the alcohol and 32 cc. of conc. hydrochloric acid was boiled under a reflux condenser for 4 hours, with the further addition of 10 cc. of the acid during this operation. The mixture was homogeneous at first, but soon separated into 2 layers. The chloride was washed thoroughly, dried, and distilled.

Analysis. Calc.: Cl, 23.25. Found: 22.96.

The Bromide, Butyl Mercapto-ethyl Bromide.—This compound was prepared in several slightly different ways. (1) A mixture of 30 g. of the alcohol and 72 g. (2 molecules) of constant-boiling hydrobromic acid was boiled for 8 hours; yield, 13 g. (2) Dry hydrogen bromide was passed for 3 hours into 50 g. of the alcohol which was kept cold; yield, 20 g., or 27%. (3) Dry hydrogen bromide was passed for 3 hours into a mixture of 50 g. of the alcohol and a little red phosphorus kept at a temperature of 30–40°; yield, 30 g., or 41%. (4) A mixture of 90 g. of the alcohol and 125 g. of constant-boiling hydrobromic acid (3.5 molecules) was boiled for 3 hours under a reflux condenser; yield, 68 g., or 51%. In all cases the layer of bromide was separated, washed carefully, and distilled.

Analysis. Calc.: Br, 40.57; S, 16.28. Found: Br, 40.40; S, 15.93.

Dibutyl Ethylene Sulfide, $\text{BuSCH}_2\text{CH}_2\text{SBu}$.—To a solution of 5 g. of sodium in 100 cc. of alcohol, 20 g. of butyl mercaptan and 40 g. of the bromide just described were added. The mixture was refluxed for a time, water was added, and the oily layer was separated, dried and fractioned. The main portion boiled at 130° at 5 mm. pressure and proved identical with a product, to be described later, which was obtained by the action of ethylene bromide upon butyl mercaptan.

Vinyl-butyl Sulfide.—To 75 cc. of alcohol in which 6 g. of sodium had been dissolved, 35 g. of the bromide was added and the mixture was heated for 30 minutes. Water was added and the oily layer washed and dried. Under atmospheric pressure, this began to distil at 150°, but the boiling point rose steadily to 217°. Helfrich and Reid¹ had a similar experience with vinyl sulfide. Several preparations were made, but no material of constant properties could be obtained. That vinyl-butyl sulfide was present seems to be shown by the following experiments. Bromine was absorbed rapidly by a chloroform solution but the desired dibromide could not be obtained; complicated reactions appear to take place. A chloroform solution of the product was saturated with hydrobromic acid. After the solution had stood during the night, it was saturated with hydrogen bromide again. When the chloroform was removed and the product had been fractioned in vacuum, an oil boiling at 75° under 4 mm. pressure was obtained, d_4^{20} 1.2253, and d_{25}^{25} 1.2075, and contained 40.38% of bromine instead of 40.57 as calculated for the monobromide. Since the density does not agree with that of the original primary bromide, it was hoped that it might be the secondary

¹ Helfrich and Reid, *J. Am. Chem. Soc.*, **42**, 1225 (1920).

bromide, BuSCHBrCH_3 , which, according to Markownikow's rule,¹ would be expected. To test this conclusion, the product was made to react with the sodium compound of butyl mercaptan as described above. A bis-sulfide was obtained, which boiled at $106-7^\circ$ at 3 mm. This, on oxidation, gave a sulfone melting at 180° which is known to be $\text{BuSO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{Bu}$, instead of the sulfone $(\text{BuSO}_2)_2\text{CHCH}_3$ which melts at 64° . This showed that hydrobromic acid had added to regenerate some at least of the original primary bromide. Since the yields of these sulfones are always low, the presence of some of the isomeric bromide is not excluded.

The Iodide.—An attempt was made to obtain this compound by allowing a mixture of 15 g. of the chloride, 20 g. of sodium iodide and 80 cc. of alcohol to stand during the night. Water caused the formation of an oily layer which was washed, and dried over calcium chloride. This liquid contained 41.89% of iodine instead of 52.02% calculated for the iodide. An attempt was made to distil it *in vacuo*, but decomposition took place accompanied by deposition of iodine on the sides of the flask. A viscous oil was left as a residue. This was washed with a solution of thiosulfate and the iodine in the residual oil was determined. The iodine content was found to be 76.33%, which agrees with 76.48% calculated for $\text{C}_4\text{H}_9\text{SI}_2\text{CH}_2\text{CH}_2\text{I}$, though this agreement is regarded as largely accidental in view of the properties of the residue. Rathke² has prepared an analogous compound, $(\text{C}_2\text{H}_5)_2\text{SI}_2$.¹

The peculiar difficulty encountered with the iodide may be related to the known tendency of sulfides to form sulfonium compounds with alkyl iodides. A complicated sulfone might be formed by the union of the iodide with itself. This would be decomposed by heat, and liberated iodine might combine with some of the iodide.

Summary.

The following compounds have been prepared: $n\text{-C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{OH}$, butyl mercapto-ethyl alcohol; $n\text{-C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{OCOCH}_3$, butyl mercapto-ethyl acetate; $n\text{-C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{Cl}$, butyl mercapto-ethyl chloride; $n\text{-C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{Br}$, butyl mercapto-ethyl bromide.

SOME DERIVATIVES OF BUTYL MERCAPTAN AND THEIR MERCURIC IODIDE COMPOUNDS.

Most of the investigations concerned with mercaptans have been limited almost exclusively to the lower members of the series, *viz.*, to methyl and ethyl mercaptans. The following investigation was undertaken to extend our knowledge to the higher members of the series, particularly to normal butyl mercaptan and to accumulate further information about compounds which contain the sulfide grouping more than once, or this group with other groups.

¹ *Ber.*, 2, 660 (1869); *Ann.*, 153, 256 (1870).

² Rathke, *Ann.*, 152, 214 (1869).

The work may be divided into 2 parts: compounds prepared by the action of the sodium salt of butyl mercaptan with halides; and those prepared from butyl mercaptan with aldehydes or ketones.

The sulfones of these sulfides, as well as their mercuric iodide compounds, have been prepared, partly for their own sakes and partly to furnish solids for identification and for analysis.

Experimental.

Reactions with Halides.

The mercaptan was dissolved in from 3 to 5 parts of 95% alcohol, together with an equivalent amount of sodium hydroxide, and to this mixture the calculated amount of the halide was added. The mixture was heated till the reaction seemed to be complete, diluted with water, and the oil separated. From the less volatile oils, impurities were eliminated by steam distillation. The oils were dried over calcium chloride and fractioned, usually *in vacuo*. It is hard to give yields on account of distillation losses, but they were all fairly good. The halides used were ethyl iodide, methylene chloride, ethylene bromide, chloro-methylethyl ether and phenacyl chloride. The following compounds have been prepared: ethylbutyl sulfide; methylene dibutyl sulfide or dibutyl mercapto-methane; ethylene dibutyl sulfide or α,β -dibutyl mercapto-ethane; ethoxy-methyl-butyl sulfide; and butyl phenacyl sulfide. Their properties are given in Table I.

TABLE I.

Formula.	B. p. ° C.	d_4^{20} .	d_{25}^{25} .	n_D^{20} .
$C_2H_5SC_4H_9$	144-5	0.8763	0.8574	1.6527
$C_4H_9SCH_2SC_4H_9$	146 at 43 mm.	0.9482	0.9332	1.4964
$C_4H_9SCH_2CH_2SC_4H_9$	129-30 at 5 mm.	0.9524	0.9389	1.4962
$C_2H_5OCH_2SC_4H_9$	179-81	0.9054	0.8877	1.4502
$C_4H_9COCH_2SC_4H_9$	140 at 3 mm.	1.0712	1.0589	1.5050

Reactions with Aldehyde and with Ketones.

The reactions of butyl mercaptan with aldehydes and with ketones were all carried out under the same conditions. The aldehyde, or ketone, was mixed with 2 equivalents of the mercaptan and the mixture heated to 50-60° under a reflux condenser for several hours, while a slow current of dry hydrogen chloride was passed into the liquid. With acetaldehyde, application of heat was not required. Water was added to the product, which was then distilled with steam to rid it of volatile impurities. The residual oil was separated, dried over calcium chloride and fractioned *in vacuo*. The yields of purified products were 50 to 60% of the calculated amounts. The following compounds have been prepared: acetaldehyde-dibutyl mercaptal; acetone-dibutyl mercaptol; benzaldehyde-dibutyl mercaptol; and acetophenone dibutyl mercaptol. Their physical properties are given in Table II.

TABLE II.

Formula.	B. p. ° C.	d_0^0 .	d_{25}^{25} .	n_D^{20} .
$\text{CH}_3\text{CH}(\text{SC}_4\text{H}_9)_2$	105 at 3 mm.	0.9399	0.9272	1.4900
$(\text{CH}_3)_2\text{C}(\text{SC}_4\text{H}_9)_2$	110 at 4 mm.	0.9304	0.9215	1.4842
$\text{C}_6\text{H}_5\text{CH}(\text{SC}_4\text{H}_9)_2$	167 at 4 mm.	1.0180	0.9999	1.4445
$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{SC}_4\text{H}_9)_2$	167-8 at 3 mm.	1.0241	1.0110	1.5535

Sulfones.

Dibutyl Sulfone Methane, $\text{C}_4\text{H}_9\text{SO}_2\text{CH}_2\text{SO}_2\text{C}_4\text{H}_9$.—Various methods of oxidation were tried, but none was found entirely satisfactory; the yields were generally poor.

Four g. methylene dibutyl sulfide was added to 150 cc. of water containing 16 cc. of sulfuric acid and 25 g. of sodium dichromate. A vigorous reaction took place, after which the mixture was boiled for 45 minutes. As the liquid cooled, the sulfone separated. After recrystallization from hot water, it formed large white plates. The same product was obtained when 5 g. of the sulfide was dropped into 20 cc. of fuming nitric acid. The sulfone separates when this mixture is poured into water. The yield was about 2 g. by each method. The melting point is 182° .

Calc.: S, 25.03. Found: 25.06.

Ethylene Dibutyl Sulfone, $\text{C}_4\text{H}_9\text{SO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{C}_4\text{H}_9$.—Ten cc. of the sulfide was added slowly to 20 cc. of fuming nitric acid, while the acid was cooled and stirred. When this product was poured into water, 25 g. of the sulfone separated. Recrystallized from hot water, it melted at 180° .

Calc. : S, 23.73. Found: 23.65.

Ethylidene Dibutyl Sulfone, $\text{CH}_3\text{CH}(\text{SO}_2\text{C}_4\text{H}_9)_2$.—While a suspension of 5 g. of the sulfide in 300 cc. of 2% sulfuric acid was stirred rapidly, a 5% solution of potassium permanganate was added to it slowly till the pink color was permanent; then sodium sulfite was added to dissolve manganese dioxide. The solution was evaporated to $\frac{1}{3}$ its volume, filtered and cooled. This caused the separation of the sulfone as white needles. It melts at 64° .

Calc.: S, 23.73. Found: 23.97.

Benzylidene Dibutyl Sulfone, $\text{C}_6\text{H}_5\text{CH}(\text{SO}_2\text{C}_4\text{H}_9)_2$, was prepared by the same method. Yield, 0.2 g. from 5 g. of sulfide; m. p., 86° . A better yield (0.4 g from 3 g.) is obtained if a solution of the sulfide in 60 cc. of acetic acid is treated first with water until an incipient turbidity appears, and then slowly with pulverized permanganate. Occasionally some dil. sulfuric acid should be added. When the calculated amount of permanganate had been used the solution was diluted with 100 cc. of water, cooled and filtered. The precipitate was extracted with boiling water from which the sulfone crystallized as white needles. This is a modification of the method employed by Hilditch.¹ No sulfones could be obtained from

¹ Hilditch. *J. Chem. Soc.*, 93, 1524 (1908).

the mercaptols made with acetone and with acetophenone; oxidation to sulfonic acids must have taken place. When the sulfur atoms are separated by 2 carbon atoms, $\text{RSCH}_2\text{CH}_2\text{SR}'$, strong oxidizing agents may be used.

Though all of the oxidation methods mentioned above were tried sulfones were not obtained from ethoxy-methyl-butyl sulfide, acetone-dibutyl mercaptal and acetophenone dibutyl mercaptol.

Mercuric Iodide Derivatives.

It was expected that mercuric iodide would combine with these sulfides 1:1, but, except for the 2 sulfides, methylene dibutyl sulfide and ethylene dibutyl sulfide, this was found not to be the case. In all other cases the ratio of iodine to mercury in the product was less than 2:1, which implies that combination takes place with mercuric rather than with mercurous iodide. Except for ethyl-butyl sulfide, 2 mercuric iodide groups are taken up for each atom of sulfur present. A part of the iodine may enter the molecule by substitution and the other part remains in the mother liquor from which the compounds separate. In a number of instances these mother liquors were titrated for iodine and, in all cases, very nearly the calculated amount of iodine was found. They were found to be acid to litmus. The mother liquors from the 2 compounds with mercurous iodide mentioned above, contained no iodine.

To prepare these compounds, 2 to 5 g. mercuric iodide was suspended in 50 cc. of acetone, and the sulfide was added slowly while the mixture was shaken and cooled. The disappearance of red mercuric iodide determined the end of the reaction. This required about 2 mols of the sulfide to 1 mol of the mercuric iodide in the first 5 preparations and about 1:1 for the other 4. Sometimes white or yellow crystals appeared immediately, while in some cases the addition of alcohol was necessary to precipitate the compound.

The compounds which separated readily from acetone were recrystallized from it, the others, from alcohol.

The compounds and their analyses are given in Table III.

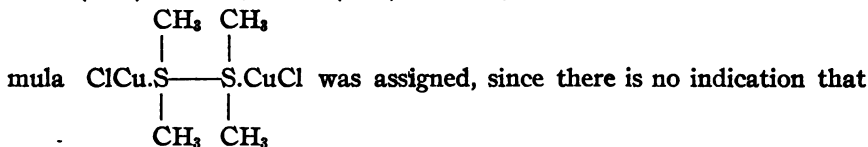
TABLE III.

Compound.	Color and form.	M. p. C.	Hg calc. %.	Found. %.	I calc. %.	Found. %.
$2\text{C}_2\text{H}_5\text{SC}_2\text{H}_5, 3\text{HgI}_2$	white plates	163	49.38	49.14	32.06	32.33
$\text{C}_4\text{H}_9\text{SCH}_2\text{SC}_2\text{H}_5, \text{HgI}_2$	small cryst.	89	31.02	30.85	39.26	39.22
$\text{C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{SC}_2\text{H}_5, \text{HgI}_2$	white plates	85	30.36	30.41
$\text{C}_2\text{H}_5\text{OCHISC}_2\text{H}_5(\text{HgI})_2$	yellow plates	156	43.16	43.42	40.98	41.17
$\text{C}_4\text{H}_9\text{COCH}_2\text{SC}_2\text{H}_5(\text{HgI})_2$	yellow plates	158	46.48	46.60	29.41	29.67
$\text{CH}_3\text{CI}(\text{SC}_2\text{H}_5)_2(\text{HgI})_4$	yellow plates	138	48.86	48.83	38.65	38.44
$(\text{CH}_2\text{I})_2\text{C}(\text{SC}_2\text{H}_5)_2(\text{HgI})_4$	yellow plates	159	45.30	45.50	42.97	42.68
$\text{C}_4\text{H}_9\text{CI}(\text{SC}_2\text{H}_5)_2(\text{HgI})_4$	yellow plates	86	47.08	47.17	37.23	36.93
$\text{C}_4\text{H}_9(\text{CH}_2\text{I})\text{C}(\text{SC}_2\text{H}_5)_2(\text{HgI})_4$	yellow plates	155	46.72	46.84	36.93	36.75

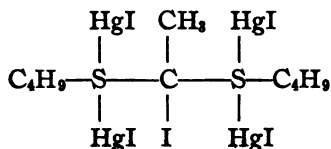
The sulfur in (1) was found to be 5.05, calc. 5.26%; and in (4) 3.45, calc. 3.33%.

Discussion.

Phillips¹ has observed that methyl sulfide and cupric chloride do not form $(\text{CH}_3)_2\text{S} \cdot \text{CuCl}_2$, but $2(\text{CH}_3)_2\text{S} \cdot 2\text{CuCl}$, to which the structural for-



the copper has been reduced. Similarly, auric chloride unites with the same sulfide to form $\text{ClAu} \cdot \text{S}(\text{CH}_3)_2$. We may assume, with Phillips, that the sulfur in our compounds has a valence of 4 and write:

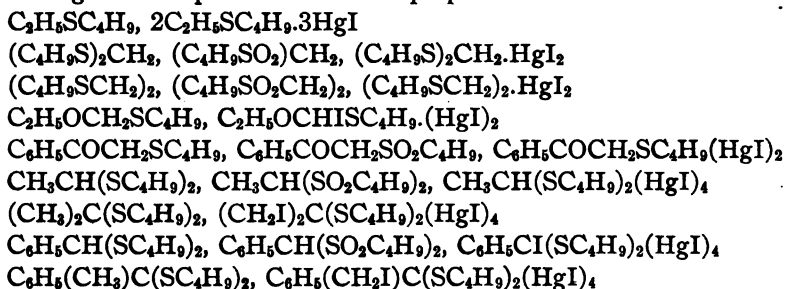


Tschugaeff² has obtained crystalline derivatives of the type $\text{CuCl} - \text{RSCH}_2\text{CH}_2\text{SR}$ which correspond with 2 of ours.

The only compound of a new type which we obtained is represented by the formula $2\text{C}_2\text{H}_5\text{SC}_4\text{H}_9 \cdot 3\text{HgI}$, obtained from ethyl-butyl sulfide, which is similar to $2(\text{CH}_3)_2\text{S} \cdot 3\text{HgCl}_2$ obtained by Phillips, except that in this case we have mercuric iodide instead of mercurous iodide.

Summary.

A number of derivatives have been made from butyl mercaptan. The following new compounds have been prepared:



¹ Phillips, *J. Am. Chem. Soc.*, **23**, 256 (1901).

² Tschugaeff, *Ber.*, **41**, 2226 (1908).

BIOGRAPHY.

Thomas Cobb Whitner, Jr., was born at Atlanta, Georgia, February 7, 1893. His elementary education was received in the schools of that city. He entered the Georgia School of Technology in 1909, from which he received the degree of Bachelor of Science in Textile Engineering in 1914. Two more years of study were spent at this same institution for which he received the degree of Bachelor of Science in Chemistry in 1916. In 1917 he entered the Johns Hopkins University as a graduate student and has continued his studies in Chemistry at this University for the past three years.

Gaylord Bros.
Makers
Syracuse, N. Y.
PAT. JAN. 21, 1908

YC 39916

QD305
462004 A4W5

W. F. Putnam

UNIVERSITY OF CALIFORNIA LIBRARY

